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A model for the zeta potential of copper sulphide

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Abstract

A model is proposed for the zeta-potential versus pH curve of Covellite (CuS). The classical Gouy-Chapman-Stern treatment of the adsorption of protons is applied to a model surface derived from the crystallographic data. The surface charges are obtained by an original adaptation of the concepts from the MUSIC model to a sulphide, i.e. the analysis of the chemical bonding in Pauling's electrostatic valence framework to derive partial surface charges. The authors develop a software for the fitting of $p\zeta$ -pH curves using IPHREEQC for the calculation of the zeta potential at each pH point and MATLAB to drive the calculation of the whole pH set and the optimisation of the parameters: capacitances of the double layer, site densities, charges and acidity constants. The model successfully reproduces the experimental data, considering only two sulphided surface sites: introduction of an elemental sulphur layer or consideration of hydroxyl surface sites is not required to explain the charging behaviour of Covellite when carefully precipitated under nitrogen.

Keywords: Copper Sulphide, Zeta potential, Model, MUSIC, IPHREEQC, MATLAB

1. Introduction

1.1. Background

Acid Mine Drainage (AMD) has been one of the most prevalent sources of environmental pollution in regions of high mineral extraction activity "The low pH that characterises most AMD contaminated wastewater induces leaching of minerals which may lead to heavy impregnation of various metal ions" [1]. A conventional method of dealing with AMD has involved the use of lime which results in neutralisation of the waste water and the simultaneous precipitation of the metal ions as hydroxides. According to Dyer and co-workers [2] and Charerntanyarak [3], the minimal hydroxide solubility from AMD is achieved at an approximate pH range of 9.5-10. Consequently, this means that maximum metal ion removal from AMD using hydroxide precipitation is only possible in this pH range. In order to promote optimal metal hydroxide precipitation, large amounts of lime have to be added so as to attain this relatively high pH.

Metal sulphide precipitation has been proposed as an alternative to hydroxide precipitation due to several

advantages over the latter that include: relatively lower solubilities which result in much lower downstream metal ion concentrations; potential selective recovery which would promote re-use of metal ions and a significant reduction in volume of the residual waste stream [4]. However, the same attributes that render metal sulphide precipitation superior to hydroxide precipitation also confer challenges to the overall viability of the process. The significantly low solubilities of metal sulphides result in the sulphide precipitation processes being inherently driven by high supersaturation. It has become generally accepted that the pre-requisite for the production of non-colloidal metal sulphide particles is to operate under mildly supersaturated conditions [5],[6] and hence the high supersaturation conditions that characterise metal sulphide precipitation promotes the production of colloidal particulates. In a sedimentation or filtration based separation process the production of colloidal particles results in the sub-optimal solid liquid separation of precipitated material which severely compromises the efficiency of the overall process. Some electrochemical studies have shown that copper

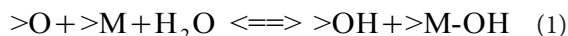
sulphide particles possess a highly negative zeta potential at pH values greater than 2, [7] and [8]. According to the DLVO theory, [9] and [10], this results in colloidal stability and a decrease in the absolute value of the zeta potential is required to promote aggregation and consequent enhanced separation. The exact value of this threshold zeta potential varies from one metal sulphide system to another largely due to the different Hamaker constants [11]. Other factors that also influence stability are ionic strength and solid fraction. According to Ottewill [12], aggregation should generally be dominant within a zeta potential range of -15 mV to +15 mV. This is consistent with results presented by Mokone and co-workers [7], the authors attributed the stability of a precipitated copper sulphide suspension to a highly negative zeta potential of about -38 mV at a pH of 6 while Vergouw and co-workers [13] also showed that the maximum settling velocity for PbS and FeS was observed roughly coincident to the isoelectric point.

It is from this background that the importance of electrochemical knowledge of metal sulphide particles is crucial in predicting and understanding suspension behaviour of metal sulphide systems. Work carried out by Moignard and Healy [14] led to the initial development of a deduction that characterised the surface of metal sulphide particles of being composed of two functional groups, a sulphido- group (>SH) and a hydroxo- group (>OH). The charge on the surface of a metal sulphide particle, therefore, becomes dependent on the density and partial charge of the surface sulphido- and hydroxo- groups respectively. Surface density and partial charge of the surface groups depend on the crystal lattice structure and the interaction between the respective metal and sulphide ions. Hiemstra and co-workers [15] developed a charge distribution and multi-site complexation model (CD-MUSIC) which can be used to determine the surface charge of (hydr)oxide species. The model can predict the zeta potential-pH properties of oxide and hydroxide species and this knowledge is invaluable in various geological, agricultural and precipitation studies. In the current study the CD-MUSIC model will be used to develop a surface complexation model that is applicable to the surface of metal sulphides. This will be done by adapting the similarities that exist between the two systems and in certain cases proposing original ideas based on first principles of physical chemistry.

1.2. Modelling of p ζ -pH curves: state of the art

Because of the importance of oxide and hydroxide compounds in geochemistry, transport of metal ions in soils and industry (intermediates, pigments, fillers, catalysts, ceramics etc.), their respective properties

have been widely studied. The available literature is too extensive to be cited here and many good textbooks have been published (e.g. [16]). There is general consensus that the aqueous surface of (hydr)oxides is covered by >O and >OH sites (where >X denotes a species X, bound to a surface, and can represent either Cu, S, O or any cation M) and this can be i) lattice oxide or hydroxide ions with unsaturated coordination at the surface; ii) a result of the adsorption of water on coordinately unsaturated metal and oxide ions at the surface. The latter gives rise to different hydroxyl groups according to Equation (1):



Consequently, even the simplest surfaces such as MgO {001} bear at least two different hydroxyl sites. More complex structures with structurally different faces and several metal and/or oxide sites exhibit wide variation in the nature of surface hydroxyl groups [17]. The surface charge then arises from the protonation/deprotonation of these surface hydroxyl sites and this is classically ruled by pKa acidity constants. Therefore, it follows that surface hydroxyl groups in different structural environments exhibit different acidity constants [18]. This means that the knowledge of pKa values is crucial in predicting surface charge and rightfully so it has been the object of many studies, especially by ab-initio methods [19]. Currently the most successful approach is the straightforward MUSIC model, [15] and [20], which is based on two main original concepts: i) an empirical relation between the geometrical environment and the pKa; ii) a partial charge on the less or more protonated hydroxyl as derived from Pauling's electrostatic valence.

The calculation of the surface charge of a particle in an aqueous solution of known pH requires additional input of the electro-chemical potential of surface species which is derived from the electrostatic potential which itself arises from the presence of charged surface species. A classical treatment to this challenge is the use of the Poisson-Boltzmann equation and its resolution in the framework of a double layer or triple layer, typically the Gouy-Chapman-Stern (GCS) theory. Derived from the same theory is the value of the potential at the (ill-defined) shear plane in the motion of charged particles in an electrostatic field: namely the zeta-potential (p ζ) that is easily computed from the experimental electrostatic mobility measured by commercial "zetameters".

A combination of non-integer surface charges, multiple surface pKas and the GCS theory are state of the art and implemented in software such as PHREEQC [21] to successfully model the p ζ of oxides in various environments [22] and [23]. GCS calculations but with "conventional" charges (>S-, >SH, >SH2+) have been

performed on some sulphides such as ZnS [24] and FeS [25], but no literature on CuS has been found except for a few raw p ζ -pH, mobility-pH or charge-pH curves [8], [26] and [7].

2. Materials and methods

2.1. Reagents

All chemicals used in the investigation, CuSO₄·5H₂O, Na₂S·9H₂O, KCl, NaOH and HCl were of analytical grade obtained from Sigma Aldrich and these were used without further purification. Solutions were made up to the required concentration using Millipore de-ionised water. All gases used were obtained from Afrox and regulated to one atmosphere during use. Nitrogen was at a purity level of 99.999 %.

2.2. Experimental set-up

Precipitation of copper sulphide was carried out at room temperature (20°C) and atmospheric pressure. A 1 L glass vessel, fitted with baffles and operated as a continuously stirred tank reactor (CSTR) was used as a metal to sulphide contactor. The reaction vessel was covered at the top with a lid that had 7 ports for a sulphide resistant pH probe, Redox probe, overhead stirrer, reagent feed, nitrogen sparger and an acid base dosing port. Agitation in the vessel was achieved by a 45° pitched 4 blades impeller connected to an overhead variable speed motor operating at 650 rpm. The reagents were pumped into the reactor using calibrated Watson Marlow 520S (Falmouth, UK) pumps. An automatic dosing unit, Metrom 800 Dosino Unit (Switzerland), was used to control pH of the reaction vessel by addition of either 0.5 M HCl or 0.5 M NaOH. Redox potential was measured using a Pt and Ag/KCl probe from Metrohm AG (Switzerland). A ring sparger was used for the delivery of nitrogen into the reaction vessel.

2.3. Analytical techniques

A dynamic back light scattering technique (Malvern Zetasizer Nano ZS model) was used to measure the zeta potential of the particles. The p ζ -pH curves were produced using the MPT-2 Autotitrator in conjunction with the Malvern Zetasizer Nano. The autotitrator was connected to a sulphide resistant pH probe which was inserted into the sample measurement cell. Sample pH adjustment was achieved by the addition of either 0.2 molar HCl or 0.2 molar NaOH.

2.4. Experimental procedure

The CSTR was filled to the mark with de-ionised water after which the overhead stirrer was switched on. Nitrogen gas was then sparged through the reactor for 30 minutes before the reagents were pumped into the reactor simultaneously via the peristaltic pumps.

The reagent flowrate was kept constant at 0.5 L·min⁻¹ throughout the experiment for both the reagents. Fluctuations in reagent flowrate were monitored using customised graduations on the stock solution vessels. In the case of flowrate variation between the metal ion stream and sulphide ion stream, the experiment was aborted. Oxygen contamination in the stock solution vessels was prevented by continuous nitrogen sparging. The pH was controlled at pH 6 throughout the entire experiment and the redox potential was recorded after every 2 minutes. Steady state was achieved after about 30 minutes. All samples containing copper sulphide particles were collected after the attainment of steady state.

A previous study, performed in the same precipitation conditions, showed that the X-Ray Diffraction pattern exhibit only the covellite peaks, broadened consistently with a crystal size of about 5 nm [27].

2.5. Calculations

Modelling of the experimental pz-pH curves was performed using Matlab R2012b (www.mathworks.com/products/matlab/), IPhreeqcCOM 3.0.0.-7430 and the original software described in section 3.3.

3. Theory

3.1. Transposition of the MUSIC model to CuS

The MUSIC model, originally derived for oxides, [15] and [20], predicts surface properties based on input of surface site information such as the local geometry and the partial charge. Incorporating the surface site density to the model then gives the collective net interaction of the sites to which the outcome is considered as the particle surface charge. According to the MUSIC model, prediction of surface acidity constants is based on an empirical correlation that cannot be derived for sulphides because of the lack of data on the acidity constants of sulphido complexes of metals in aqueous solution. In contrast, the structural data used to derive the partial charge of surface sites of (hydr)oxides compounds based on Pauling's electrostatic valence, can also be applied similarly in the case of sulphided surface sites of Covellite. In order to calculate this partial charge two steps are necessary: i) assign the electrostatic valence of surface sites in the Covellite structure; ii) calculate the resulting surface charges:

3.1.1. Electrostatic valence in Covellite

3.1.1.1. Pauling's electrostatic valence

Pauling [16] introduced the electrostatic valence (v) or strength of the electrostatic bond of an ionic solid as:

$$v = z_{\text{cat}} / v_{\text{cat}} \quad (2)$$

where z_{cat} is the charge on the cation and v_{cat} is its

coordination.

He postulated the electrostatic valence rule, also known as Pauling's second building rule, which can be defined according to the original statement as: "in a stable ionic structure the valence of each anion, with changed sign, is exactly or nearly equal to the sum of the strengths of the electrostatic bonds to it from the adjacent cations".

This can be defined according to Equation (3):

$$-z_{an} = v_{an} \cdot v \quad (3)$$

where subscript an holds for the anion. A proof of this postulate was given in [19] and as a consequence, another formulation for a binary ionic solid is:

$$v = z_{cat} / v_{cat} = z_{an} / v_{an} \quad (4)$$

Though Pauling only used the concept as a building rule, many authors, including [28] and [15] considered, from the name by Pauling "strength of the electrostatic bond" that v (originally s in "The nature of the chemical bond") is related to some kind of the amount of electron exchange or charge compensation in a cation-anion pair. Thus, in a complex solid, where a cation has different first neighbours (different element or different structural element), we can define different electrostatic valences for the same cation and its different neighbours (idem for one anion), provided that the electrostatic valence rule is satisfied.

3.1.1.2. Coordinences of ions in Covellite

The structure of Covellite [29] (Figure 1) shows the stacking of two distinct layers along the z-axis and named according to the authors as, "Cu₃-S -CuS₃" and "S₂" layers:

- "Cu₃-S -CuS₃" are one atom thick and each Cu ion has three S neighbours in the plane and each S ion has three Cu neighbours in the same plane and two Cu neighbours in the adjacent "S₂" layers (one beneath, one above);

- "S₂" layers, with a "core" of S₂ ions, stacked parallel to the z-axis, topped by copper ions (beneath and above). Each S₂ ion has six Cu neighbours in the layer and each Cu ion has three S₂ neighbours in the layer plus one S ion neighbour in the adjacent "Cu₃-S -CuS₃" layer.

The coordinences of the four building units are given in Table 1.

3.1.1.3. Charges on ions in Covellite

In addition to complex coordination, Covellite exhibits a complex electronic structure. It is an ionic solid with metallic conductance [30]. According to Goh [31] [32], the best representation should be: Cu⁺³(S₂²⁻)₂ S₂^{h+} where h⁺ is a hole (electron vacancy). There is a general agreement that the oxidation degree of copper is Cu(I) and the hole is localised on S or S₂ ions. This is supported by ab-initio calculations where the contribution to the levels close to the Fermi level come mostly from S(3p) orbitals [33]. The localisation of the

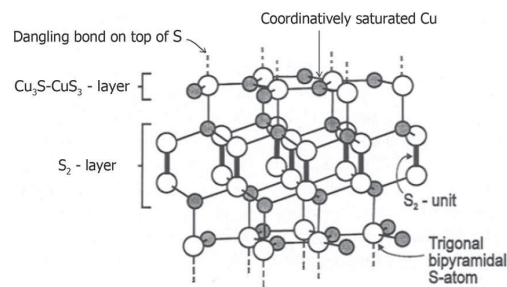


Figure 1: Structure of Covellite (ref [29], reproduced with permission and modified)

Element	Layer	Species	Relative abundance of species	Partial charge	Electrostatic valence	
					intra-layer	inter-layer
Cu	Cu ₃ S-CuS ₃	Cu	1	1	1/3	0
	S ₂	Cu	2	1	(1+x)/6	(1-x)/2
S	Cu ₃ S-CuS ₃	S	1	-2+x	1/3	(1-x)/2
	S ₂	S ₂	1	-1-x	(1+x)/6	0

Table 1: Charges, coordinences and electrostatic valences in Covellite

holes between S ions in "Cu₃-S -CuS₃" and "S₂" is not ascertained by the literature, and we will consider as a parameter the fraction, x , of holes on S ions in the "Cu₃-S -CuS₃" layer. The corresponding charges are reported in Table 1.

3.1.1.4. Values of electrostatic valences in Covellite

The Cu(I) ion in the "Cu₃-S -CuS₃" layer has a well-defined charge of (+1) and a coordination of (3): the respective electrostatic valence, therefore, is 1/3. Consequently the S_{x-2} ion in the "Cu₃-S -CuS₃" layer "receives" $3 \cdot 1/3 = 1$ bond order from its neighbours in plane "Cu₃-S -CuS₃" and $2 \cdot v_2$ from its two Cu neighbours in the "S₂" layer. Hence, according to the second building rule:

$$2-x = 3 \cdot (1/3) + 2 \cdot v_2 ; v_2 = (1-x)/2 \quad (5);(6)$$

The Cu(I) ion in the "S₂" layer has a well-defined charge of (+1), one S neighbour in the adjacent "Cu₃-S -CuS₃" layer, to which it exchanges $v_2 = (1-x)/2$ and three neighbours in its layer, exchanging with them v_3 . According to the second building rule:

$$1 = (1-x)/2 + 3 \cdot v_3 ; v_3 = (1+x)/6 \quad (7);(8)$$

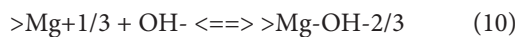
Finally, each S₂ ion has a charge of $-(1+x)$ and six Cu neighbours, which exchange with it: $v_3 = (1+x)/6$. The second building rule is satisfied by the equality:

$$(1+x) = 6 \cdot (1+x)/6 \quad (9)$$

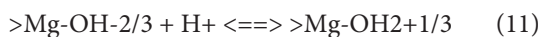
3.1.2. Surface charges in Covellite

3.1.2.1. Surface charges in MUSIC framework

The question of the charge for an atom in a molecule or a solid is a fundamental one [34] and subject of active research. A rigorous answer is given only by the combination of ab-initio calculation of the electronic density and electronic localisation function (ELF) [35] and the topological analysis of ELF [36]. Nevertheless, in the straight line of Pauling's and Yoon's [25] intuition, Hiemstra [15] proposed to consider that the charge on a surface cation is the part of its formal charge that is not compensated by the sum of strength of the ionic bonds with its nearest anionic neighbours. As an example: the formal charge on Mg in MgO is 2+, its coordinence in the bulk is 6, so the electrostatic valence is 1/3. A Mg cation on the {001} surface has one dangling bond (coordination 5 = 6-1), so its residual charge is: $2 - 5 \cdot (1/3) = 1/3$. In this framework, the charge on a species adsorbed on a coordinately unsaturated cation is modified by the value of the surface charge: e.g. OH- on Mg5c cation is $-1 + (1/3) = -(2/3)$.



The charges of protonated / deprotonated surface adsorbate are deduced from the electroneutrality, in this example:

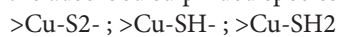


3.1.2.2. Surface structure of Covellite

It is clear from Figure 1 that Covellite has a preferential cleavage exposing {001} surfaces. This is confirmed by UHV STS/STM by [33] who, in addition, ascertain that the vertical position of the cleavage is such that the exposed planes are those named "Cu3-S -CuS3" by Patrick et al. [29].

3.1.2.3. Charge on S adsorbed on a lattice Cu ion

According to [33], the copper atoms on this surface do not show dangling bonds, which implies that bonding between "Cu3-S -CuS3" layer and "S2" layer (again named after [29]) occurs only between S atoms in the "Cu3-S -CuS3" layer and the fourth bond of a tetrahedral Cu in the "S2" layer (see Figure 1). Consequently, the effective charge on a surface Cu is null and the adsorbed sulphided species are:

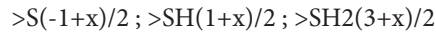


These sites can be negative or neutral, they cannot generate a positive charge at the surface of Covellite.

3.1.2.4. Charge on a surface lattice S ion

As seen in section 3.1.1.3, the dangling bond on a surface S ion on "Cu3-S -CuS3" layer has an electrostatic strength of $(1-x)/2$ where x is the fraction of holes localised on S ions in the "Cu3-S -CuS3" layer, so its residual charge is $-(1-x)/2$ and the surface protonated

species are:



These sites can generate negative or positive charge at the surface of Covellite.

3.2. Density of surface sites

According to [33], the "Cu3-S -CuS3" layer is planar, paved with regular hexagons having at their summits alternating Cu and S ions and the edge of the hexagons is 0.219 nm. The surface of an hexagon of edge a is $a^2\sqrt{3}/2$, so the density of sites is readily derived as 9.83 sites per nm² for both >Cu... and >S... sites.

3.3. Implementation of the calculations

The calculation of the zeta-potential at a given pH requires the knowledge or estimation of several parameters: densities, charges and pKas of the surface sites, ionic strength and double layer capacitance. The calculations in the Poisson-Boltzmann approximation and CD-MUSIC model are implemented in several softwares. Among these, PHREEQC [21] has some advantages: it is free and open-source, it has been validated by many published papers and the interface is easy to use after some training. In this study, we had to fit some parameters, as the pKas and charges of sites, an operation that surface modelling softwares do not operate in standard implementation. Fortunately, Charlton & Parkhurst [37] implemented a version of PHREEQC, named IPhreeqc, which is available as modules that can act as routines for other softwares. Matlab from Mathworks, Inc. "is a numerical computing environment and programming language" (<http://www.mathworks.com/products/matlab/>). Matlab allows programming in a friendly environment and includes numerical routines, e.g. "lsqcurvefit" for the adjustment of models.

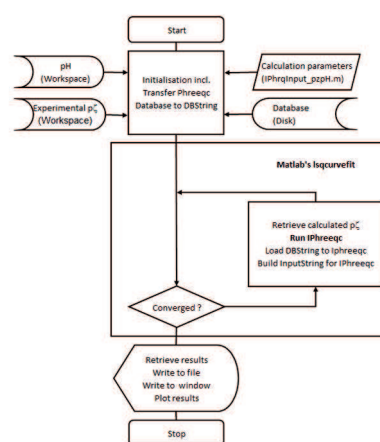


Figure 2: Calculation scheme for the optimisation of surface parameters in a CD-MUSIC model calculated by IPhreeqc with a Matlab least square optimisation routine.

This is why we developed on a Microsoft Windows 7 platform a Matlab software, having the experimental $\pi\zeta$ pH curve as an input, which runs IPHreeqc in its Component Object Model (COM) implementation and optimises the parameters of the model.

The complete scheme is described in Figure 2. The source code is given in electronic supplementary materials or on simple request to the corresponding author, under the terms of the GNU Public Licence (GPL).

Details of the implementation are given in Annex.

4. Results

4.1. Experimental results

Four precipitation experiments were carried out and the precipitated particulates were subjected to independent $p\zeta$ -pH analysis, the results are presented as run 1 to run 4 as shown Figure 3. Runs 1 to 3 (titration from high to low pH) and run 4 (titration from low to high pH) are similar, which is consistent with absence of artefact due to the precipitation of dissolved cations; nevertheless, starting from the IEP triggered agglomeration, causing some clogging in the Zetasizer internal pipes, so we used only the curves obtained by titration from high to low pH. The pH range inclusive of all runs was between a pH of 1.6 and 9 while the zeta potential range fell between a maximum of -8 mV and a minimum of -51.1 mV. By extrapolation, the iso-electric point of all 3 individual precipitations was below a pH of 1.6. In general, the zeta potential magnitude increased with an increase in pH although the rate of change declined for higher pH values above a pH of 4. Significant deviations in reproducibility were observed between pH ranges of 1.8-2.8 and also 4.5-6. In the low pH deviation range, run 2 resulted in generally lower zeta potential values in comparison to an agreement of zeta potential values between run 1 and 3. The same phenomena was observed at the higher pH deviation range but in contrast, run 1 yielded lower zeta potential values than

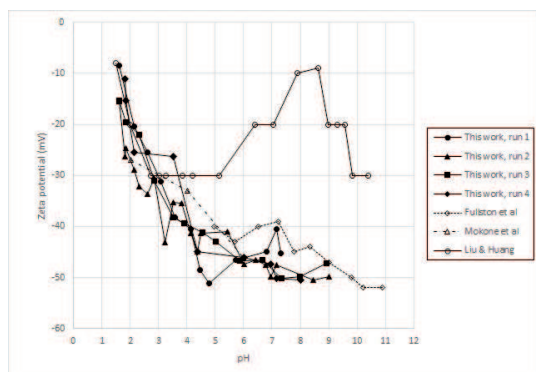


Figure 3: Measured $p\zeta$ -pH curves for CuS (Covellite), this work (run 1 to 3: from high to low pH; run 4: from low to high pH) and references [7], [8], [26].

the agreement of zeta potential values between run 2 and 3.

Work carried out by [14] showed that a low iso-electric point most likely indicates a lightly oxidised or un-oxidised metal sulphide surface. This suggests that the precipitated CuS particles under nitrogen, with a predicted iso-electric point of 1.6, can be considered as having undergone very minimal surface oxidation. This is consistent with various electrokinetic studies on CuS that have predicted iso-electric points of less than 2 [7], less than 1 [26] and less than 4 [8] (with 4 being the lowest pH investigated). As can be seen in Figure 3, the $p\zeta$ -pH behaviour of the CuS particles precipitated in this work is similar to that reported by [7] and [8]. In contrast, a large deviation is observed between the presented experimental results and those reported by [26]. The latter results show a behaviour which is consistent with surface oxidation and hence a conclusion may be made that these results represent a less “pristine” CuS surface. The slight deviations between the 3 independent experimental runs as presented in this study are characteristic of zeta potential measurements and do not in any way invalidate the general trend of $p\zeta$ vs. pH observed in Figure 3.

4.2. Modelling

4.2.1. Data selection and preparation

The three sets of experimental $p\zeta$ -pH data (see section 4.1.) were gathered in one data set. As shown on Figure 4, some points laid far from “a smooth curve” and were discarded. The authors are conscious of the arbitrary nature of such a procedure; the reason for this is that the existence of points that are obviously flawed create an impossibility to get a good fit as characterised by the R^2 : as a consequence, the fitting procedure becomes less reliable, as the hyper-surface

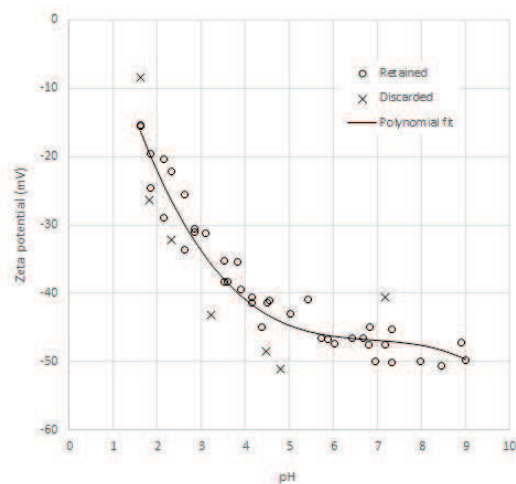


Figure 4: Pre-treatment of data for the adjustment procedure.

of R^2 versus the parameters becomes flatter. In order to limit the subjectivity of the choice of the retained points, this procedure was chosen: the whole set of ($p\zeta$, pH) points was fitted by a polynomial of degree 3 in pH using the standard functionality of MS Excel and the (7) points with a gap of more than 5 mV from the fitted curve were discarded. Subsequent modelling was performed using the original points, not the points from the polynomial fit.

4.2.2. Initial treatment

The data set prepared as described in section 4.2.1. was processed as described in section 3.3.3. with, as parameters: the capacitances of Stern and diffuse layers, charge on site #2, first pKa of site #2 and second pKa of site #1 (five parameters). Taking into account the discussion in section 3.1.2.3., the charge on site #1 was set to -2. Considering preliminary calculations, the second pKa of site 1 was set to 15 and the first pKa of site #2 to -10: this choice will be justified a posteriori

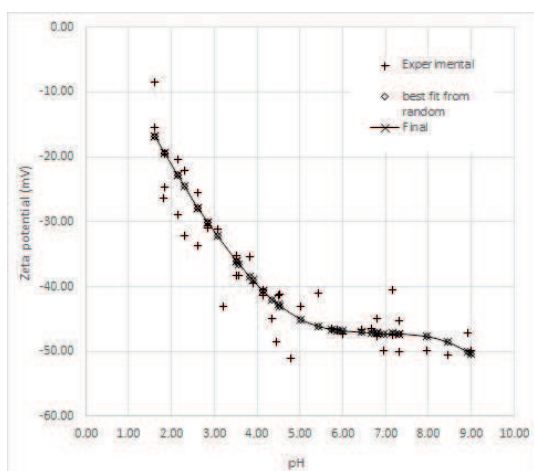


Figure 5: Experimental and modelled $p\zeta$ -pH curves for Covellite.

by the sensitivity analysis. A calculation in a 20 random starts mode in the range described in Table 2 provided as a likely global minimum the solution displayed in Table 2. Restarting the calculation from the final point of the former optimisation produces a very limited change, showing that the solution is numerically stable. The fit is satisfactory ($R^2 = 0.95$, see Figure 5). No parameter has an optimised value equal to its lower or upper bound, which justifies a posteriori our choice of bounds. This solution is used in the following section and named “best fit from random”.

4.2.3. Tuning of parameters

In this section, we describe the modifications to the “best fit from random” solution, aiming to give more

Parameter	Unit	Constant value	Lower bound	Upper Bound	Value	
					Best random	Final
Initial pH	-	1.6				
Ionic Strength	mmol/L	10				
Supporting electrolyte		KNO ₃				
Capacitance	Stern Layer	F/m ²	0.10	5.00	0.300	0.29
	Diffuse Layer	F/m ²	0.10	5.00	0.275	0.29
Site #1	Density	1/nm ²	9.83		9.83	9.83
	Charge (deprotonated)	a.u.	-2		-2	-2
	pKa1	-	-2.00	5.00	-1.56	-1.6
Site #2	Density	1/nm ²	9.83		9.83	9.83
	Charge (deprotonated)	a.u.	-0.50	0.00	-0.0157	-0.0156
	pKa1	-	-10.00		-10.00	<-2.5
>S...	pKa2	-	3.00	9.00	7.8200	8.0
R^2					0.9455	0.9459

Table 2: Calculation parameters.

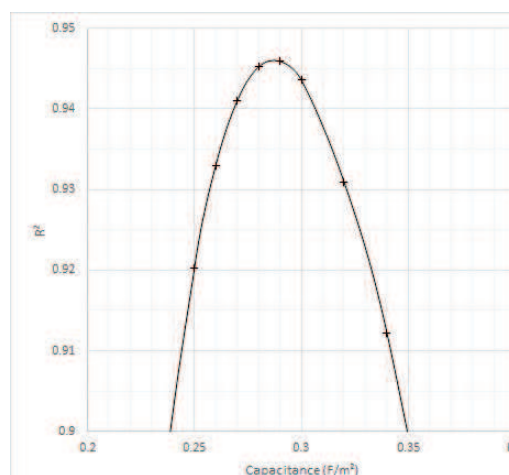


Figure 6: Sensitivity of the fit to the capacitances of Stern and diffuse layers.

physical meaning to the solution, while not forcing subjective choice.

4.2.3.1. Capacitances

The sensitivity of the fit to a change in the capacitances of Stern and diffuse layers, depicted on Figure 6, shows a maximum in R^2 about 0.29. This value, along with the optimised values from the “best fit” for other parameters, constitutes the “reference” solution and will be used as a starting point in the next sections.

4.2.3.2. Sensitivity analysis: pKas

The acidity constants for surface sites are systematically varied. Figure 7 shows that:

- the first pKa of the high coordination site $>SH_2(3+x/2) / >SH(1+x/2)$ is not critical provided it lays below -2.5;

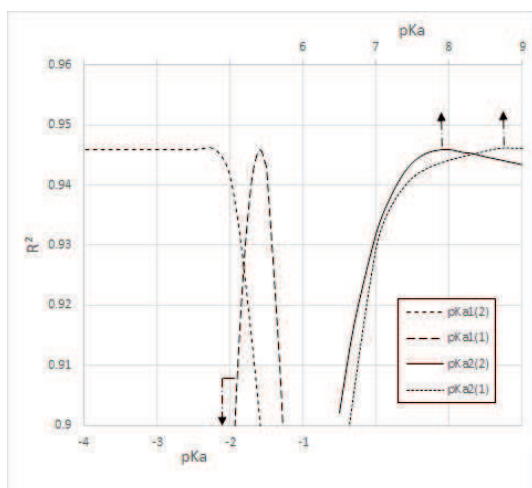


Figure 7: Sensitivity of the fit to the values of pKas.

the doubly protonated high coordination site is super-acidic;

- the adjustment is very sensitive to the value of first pKa of the low coordination site $>\text{Cu-SH}_2 / >\text{Cu-SH}-$, with a sharp maximum in R^2 at -1.6;
- the adjustment is moderately sensitive to the value of second pKa of the high coordination site $>\text{SH}(1+x/2) / >\text{S}(-1+x/2)$ with a maximum in R^2 at about 8.0;

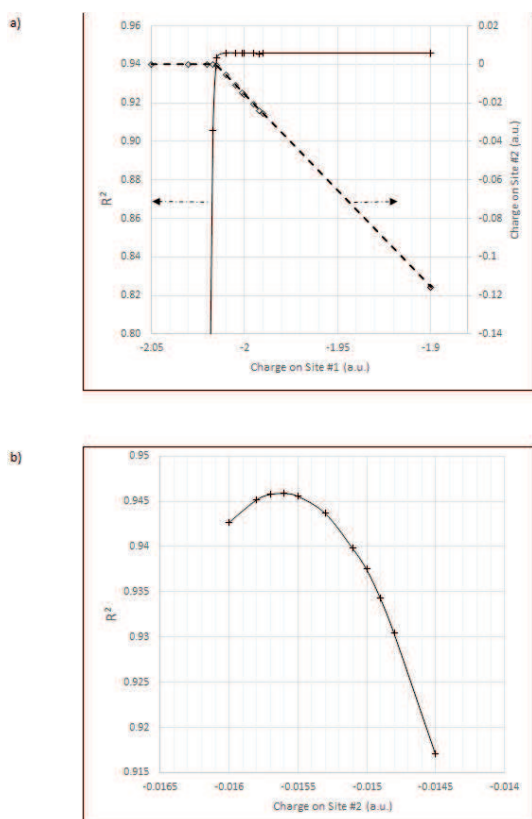


Figure 8: Sensitivity of the fit to the charges a) b).

- the second pKa of the low coordination site $>\text{Cu-SH}- / >\text{Cu-S}_2-$, is not critical provided it is higher than 9, indicating that the totally deprotonated form does not occur in the experimental pH range.

4.2.3.3. Charges

Changing the charge on site #1 only gives results with very bad R^2 , so we modify the procedure and allow the optimisation of the charge on the site #2 at each value of the charge on site #1. Figure 8 shows that the fit deteriorates fast when the charge of site #1 is taken below -2 and, on the contrary, values up to -1.9 are accommodated by a change of the charge on site #2 with no decrease in R^2 . At constant charge on site #1 equal to -2, the fit shows a sensibility to the charge on site #2, with a maximum between -0.0156 and -0.0157.

4.3. Final set of parameters for the model of Covellite p ζ -pH curve

The final optimised parameters for a model of the corresponding modelled p ζ -pH curve of Covellite are displayed on table 2 and the result on Figure 5, showing almost no difference in comparison with the “Best fit from random”.

5. Discussion

The values for the CD-MUSIC based model for the p ζ -pH curve of Covellite are physically consistent and inside the usual range, the R^2 factor has smooth variations with the values of the parameters, which is not a proof, but at least a favourable sign that the underlying hypothesis are fulfilled.

The effective charge on the high coordination site #2 is found equal to -0.0156 (a.u.), which, according to section 3.1., Table 1, is consistent with a localisation of the hole h^+ on the S ion in the “Cu3S-CuS3” layer (97%) preferentially to the S2 ion in the “S2” layer (3%). Hence, a gross formula of Covellite would be: $\text{Cu}+\text{S}-(\text{Cu}_2+\text{S}_2-2)$ or $\text{Cu}_3+\text{S}-\text{S}_2-2$, in contradiction with some ab-initio calculations [38],[33]. This discrepancy can be explained by some weakness in these calculations: the 20 years old reference [38] was based on a Tight-Binding calculation, a pioneering method that permitted the development of quantum chemistry but is now considered as obsolete; reference [33] is based on the ab-initio code Crystal95 but unfortunately using the questionable Mulliken population analysis for the calculation of charges. State of the art calculations using e.g. VASP [39] [40] should be useful to assess credible charges and the authors approached groups able to perform these calculations. As a remark: the distribution of charges from this work provides neutrality for the two layers described by Patrick [29].

Element	Material	Acid/base	Coordination of surface group (n)	pKa	Δ pKa	Partial charge on the surface cation (v)	Radius of the central element in surface group (r, nm)	$\Delta(nv/r)$	Ref
Ti	Rutile	>OH/>O	1	20.1	27.6	2/3	0.126	10.6	ii
			3	-7.5					i
		>OH ₂ /<>OH	1	6.3	27.6	2/3	0.126	10.6	i
			3	-21.3					ii
Al	Gibbsite	>OH/>O	1	23.8	21.6	1/2	0.126	7.9	ii
			3	2.2					i
		>OH ₂ /<>OH	1	10	21.6	1/2	0.126	7.9	i
			3	-11.6					ii
Fe	Hematite	>OH/>O	1	24.5	20.2	1/2	0.126	7.9	ii
			3	4.3					i
		>OH ₂ /<>OH	1	10.7	20.2	1/2	0.126	7.9	i
			3	-9.5					ii
Cu	Covellite	>SH/S	1	>9	>1	0	0.170	0.0	This work
			3	8					
		>SH ₂ /<>SH	1	-1.6	>1	0	0.170	0.0	
			3	<-2.5					

Table 3: differences in pKa for the protonation state and different coordinations.

The best value for the capacitances of the electrostatic layers is 0.29 F/m², “within the range of literature values reported for various oxides and hydroxides” [24].

As already mentioned, no pKa has been found in the literature for CuS and the literature is scarce on the determination of surface pKas of metal sulphides in general. In a one site, integer charges scheme, Zhang [24] proposes pKa = -1.1 for >ZnSH+/>ZnS which compares with -1.6 for the first pKa of the low coordination site in this work.

The differences between the two successive pKas of a same site are found >10 for both sites, which is consistent with the value of 13.8 for oxygen containing surface groups [15] and not considerably higher than the value of 6 in the serial H₂S/HS-/S-2.

The differences in acidity for the same protonation level between the two sites is >1 in each case. In the “oxide world”, the differences between sites with coordination 1 and 3 are much higher according to [15], as shown in Table 3. This can be explained by the lower electrostatic valence in Covellite compared to the mentioned oxide and by the larger size of S atom compared with O, which weakens the electrostatic interaction of the sulphide proton with metals compared to the hydroxide proton. As a single pKa is necessary from each site to model the experimental curve, one is tempted to fit the curve with a single site and two successive pKas. This is possible and the quality of the fit is good (R² = 0.972) with pKa1 = -0.6, pKa2 = 6.8, charges close to >SH₂+/>SH/>S-, Stern and diffuse layer capacitances equal to 0.38, but a density of surface sites of 3 nm⁻². The last feature is not consistent with the crystallographic data and, in addition, the surface structure clearly identifies two different sites, each with a density of 9.8 nm⁻². If the surface had a coverage of only about 15%, the trend

of cations to complete their coordination by aquation in water would create >Cu-OH groups, with a totally different p ζ -pH behaviour [12]. This is the reason why we consider the two sites above described model as more convincing.

6. Conclusion

The p ζ -pH experimental curve of unoxidised Covellite is successfully modelled by considering two sulphido surface sites having features consistently derived from the surface structure of Covellite, and does not require invoking elementary sulphur or any metal-deficient layer, nor hydroxo surface sites. This is not a proof of inexistence of these layers or sites, but an argument for a simple description of the surface of un-oxidised Covellite derived from the classical model for oxides by substitution of oxygen element by sulphur, involving >S... and >Cu-S... species.

The high quality of IPHREEQC software, permitting to develop a calculation and fitting interface in the powerful Matlab environment is a precious tool for the modelling of the charging properties of solids, including sulphides.

The basic assumptions of MUSIC, especially the derivation of partial surface charges from Pauling's concept of the strength of the electrostatic bond can be successfully applied to sulphides.

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Annex

A.1. Inputs

A.1.1. p ζ -pH experimental curve

The p ζ -pH experimental curves were available from the zetameter in Microsoft Excel worksheets and imported into the Matlab workspace as two separate vectors, e.g. “pz” and “pH”.

A.1.1.2. Parameters

The physical parameters: initial pH, ionic strength, nature of the supporting electrolyte, surface area and concentration of particles, capacitances of the Stern and diffuse layer, and for each site: element adsorbed on the site, density, charge on the deprotonated site, two pKas are entered in a specific source file (“IPhrqInput_pzpH.m”) that we will design as the input file in this paper.

In this implementation, the maximum number of sites is 4. The software can also handle inner and outer sphere complexation, but this will be the object of another paper.

The input file also contains some “technical” parameters, defining which kind of output is generated by IPhreeqc, the PHREEQC database name and directory and the options for the Matlab fitting routine lsqcurvefit.

The input file is commented with hope that the file is self-explanatory.

A.1.2. Calculation

A.1.2.1. User's point of view

The main program (“IPhrqMain_pzpH”) is called from the command line with the pH and pz vectors as arguments (“IPhrqMain_pzpH(pH,pz”).

Three modes are available from the options in the input file:

- single point calculation (“SPC”) allows the calculation of the p ζ -pH curve at the experimental pH points and the values of parameters given in the input file. It is useful in the development phase and for sensitivity analysis;

- “Fit”, where the parameters specified by a “flag” in the input are optimised to fit the experimental p ζ -pH curve. As the CD-MUSIC calculation is sensitive to aberrant values, the user must provide lower and upper bounds for the variable parameters. This is the standard mode;

- random calculation (“Ran”) performs multi-start fitting from different initial sets for the parameters, that are randomly generated inside the lower-upper bounds range for each adjustable parameter. This mode is useful to verify that the best solution from “Fit” is not a local minimum, it is computer intensive and we did not find it very useful, due to the high quality of the Trust-Region-Reflective algorithm implemented in Matlab's lsqcurvefit function.

Due to the high level of optimisation of Matlab R2012b and IPhreeqc, the calculation requires moderate time: the optimisation of the four pKas for two sites on 18 points of pH required 1 to 4 minutes on a laptop equipped with a modest Intel i3-3120M CPU at 2.50 GHz, depending on how far the initial point was from the optimum. In addition, one can run simultaneous multiple sessions of Matlab to take advantage of the multicore processors.

A.1.2.2. Technical points

The readers familiar with IPhreeqc will probably be interested by the following features.

IPhreeqc receives the informations as “Properties” that are passed through “Methods”. The call instruction is a method also. One problem arises because the properties are resident in the local workspace, not in the global one. As lsqcurvefit is a function and not a routine, its calls to IPhreeqc are in its local workspace, with this consequence: the database must be reloaded at each calculation that is launched by the optimisation routine. As a disk access at each step of the optimisation loop would be dramatic for the calculation time, the database is loaded into a string by the initialisation routine, stored through a “global” instruction, retrieved by the calling function and passed to the IPhreeqc property from the memory (By the method “LoadDatabaseString”).

The Matlab software writes a virtual Phreeqc input file for IPhreeqc into a string and passes it through the Method “RunString” at every call.

The relevant results are stored inside IPhreeqc through the input instruction “Selected_Output” and retrieved by the method “GetSelectedOutputString”.

Once in Matlab variables, the results are printed to files or to the workspace in usual I/O operations. A graph of the experimental and calculated values of the p ζ versus pH is drawn using standard functionalities of Matlab.

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